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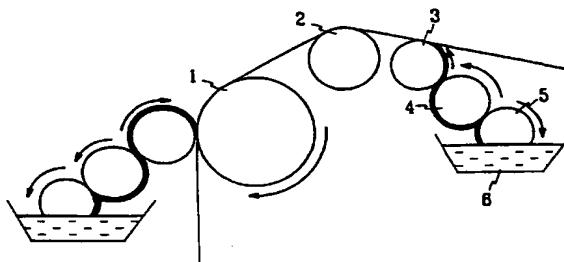
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(54) Title: RESIN-COATED STEEL SHEET FOR FUEL TANKS OF AUTOMOBILE AND METHOD OF FABRICATING THE SAME

2-5 μ m	Phenoxy Resin
50mg/m ²	Chromate film
10-40g/m ²	Zn-Ni Plate
	Cold-Rolled steel sheet



(57) Abstract: The present invention relates to a resin-coated steel sheet for fuel tanks of an automobile and a resin solution used for the same. The resin solution of the present invention comprises (a) a main solution of water soluble phenoxy resin having a number average molecular weight of 25,000 to 50,000, (b) 2 to 15 phr of melamine resin on the basis of the main solution, (c) 10 to 20 phr of colloidal silica on the basis of the main solution, and (d) water soluble ethylene-acryl resin containing 50-80 % of ethylene and 50-20 % of acryl resin and having a molecular weight of 20,000 to 50,000, in an amount of 5 to 15 phr on the basis of the main solution; and/or 0.5 to 3.0 phr of phosphoric ester on the basis of the main solution. The resin solution is coated on a cold-rolled steel sheet plated with zinc or zinc alloy over which a chromate layer films, and then dried at a local temperature of 140 to 250 °C to prepare a resin-coated steel sheet for fuel tanks of an automobile.

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RESIN-COATED STEEL SHEET FOR FUEL TANKS OF AUTOMOBILE
AND METHOD OF FABRICATING THE SAME

5

BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to an unleaded surface-treated steel sheet for fuel tanks of an automobile, more specifically, a resin-coated steel sheet coated with resin solution on the surface of unleaded surface-treated steel sheet coated with chromate layer and a method of fabricating the same.

(b) Description of the Related Art

Generally, it is required that fuel tanks for storing fuel of an automobile should have resistance to corrosion on its outer surface to be exposed to the atmosphere (hereinafter, referred to as the "cosmetic corrosion resistance") as well as resistance to corrosion on its inner surface to contact fuel such as gasoline (hereinafter, referred to as the "fuel corrosion resistance").

A fuel tank is usually made by press-forming steel sheets into cup-shaped upper and lower tank bodies, and welding the bodies to each other by resistance welding method such as spot welding or seam welding, or joining method such as soldering or brazing. In this respect, because two parts are joined each other in a fuel tank, good weldability and good processibility are required for the steel sheet to be applied for use in forming fuel tanks.

A ternesheet that is a cold-rolled steel sheet plated with lead-tin alloy has widely used as a steel sheet for fuel tanks. However, the ternesheet have been limited in its use because it contains lead that causes environmental pollution.

In this connection, extensive researches have been made to develop a surface-treated steel sheet for fuel tanks without using lead.

International patent publication No.WO 00/32843 invented by the present inventors discloses a plated steel sheet that does not use lead. The above patent provides an unleaded plated steel sheet coated with resin solution on the surface of zinc or zinc-based alloy plating steel sheet coated
5 with chromate layer to improve cosmetic corrosion resistance and fuel corrosion resistance.

The resin solution used for coating the unleaded plated steel sheet is phenoxy resin as main solution in the above invention. Since the phenoxy resin has a higher glass transition temperature (Tg) than other resins, it has
10 better characteristics such as cosmetic corrosion resistance and fuel corrosion resistance than epoxy, acryl or urethan resin in a flat plane part which is not subjected to process. However, while seam processing, phenoxy resin has a problem of decreasing cosmetic corrosion resistance and fuel corrosion resistance due to high glass transition temperature in a
15 processing part.

In order to improve the problem, there is a way to lower glass transition temperature of phenoxy resin, or to bond phenoxy resin layer and lower chromate layer chemically not to exfoliate the coating during seam processing.

20 Japanese Patent Laid Open Publication No. Hei2-18981 discloses a way to lower glass transition temperature of phenoxy resin. The above invention relates to a method for reinforcing a coating adhesion between resin and the lower part which bond to the resin by lowering glass transition temperature of phenoxy resin and modifying resin molecules to a rubber.
25 However, if the above method is applied to water-soluble resin, it is difficult to make water-soluble state when modifying it to a rubber, and to add rubber of water-soluble state into phenoxy resin of water-soluble state.

SUMMARY OF THE INVENTION

30 Therefore, the present invention is derived to solve the above

problems. The present invention provides a resin solution comprising additives lowering glass transition temperature of phenoxy resin without damaging physical characteristics of resin used for preparing resin-coated steel sheet.

5 It is another object of the present invention to provide a method of fabricating resin-coated steel sheet for fuel tanks of an automobile which can improve adhesion between phenoxy resin and matrix metal by using the resin solution.

In order to achieve the above objects, the present invention provides
10 a resin solution comprising:

(a) a main solution of water soluble phenoxy resin having a number average molecular weight of 25,000 to 50,000;

(b) 2 to 15 phr of melamine resin on the basis of the main solution;

(c) 10 to 20 phr of colloidal silica on the basis of the main solution;

15 and

(d) water soluble ethylene-acryl resin containing 50-80% of ethylene and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000, in an amount of 5 to 15 phr on the basis of said main solution; and/or 0.5 to 3.0 phr of phosphoric ester on the basis of the main solution.

20 In order to achieve the above objects, the present invention provides a resin-coated steel sheet for fuel tanks of an automobile coated with chromate film on cold-rolled steel sheet plated with a zinc (Zn) or zinc-based alloy wherein, the resin solution comprises:

(e) a main solution of water soluble phenoxy resin having a number
25 average molecular weight of 25,000 to 50,000;

(f) 2 to 15 phr of melamine resin on the basis of the main solution;

(g) 10 to 20 phr of colloidal silica on the basis of the main solution;

and

(h) water soluble ethylene-acryl resin containing 50-80% of ethylene
30 and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000,

in an amount of 5 to 15 phr on the basis of the main solution; and/or 0.5 to 3.0 phr of phosphoric ester on the basis of the main solution,

said resin solution coated on the cold-rolled steel sheet with a coating thickness of 2–10 μm after drying the resin coating.

5 In order to achieve the above objects, the present invention provides a method of fabricating resin-coated steel sheet for fuel tanks of an automobile comprising the steps of coating the resin solution of claim 1 on steel sheet and baking drying it at 160-250°C so as to have a coating thickness of 2–10 μm . The coating process of resin solution is preferably a
10 roll-coating process.

According to the present invention, it is possible to provide a steel sheet for fuel tanks which has improved coating adhesion after processing, cosmetic corrosion resistance, and fuel corrosion resistance without using lead by preparing resin solution comprising ethylene-acryl resin and
15 phosphoric ester based on phenoxy resin. Comparing to the prior Pb-Sn plating steel sheet, the present invention can effectively prevent environmental pollution. In addition, quality of a fuel tank of an automobile is improved so that it meets to the requirement of consumers.

20 **BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 is a cross-sectional view of a coating layer of the resin-coated steel sheet for fuel tanks of an automobile.

Fig. 2 is a diagram showing a bond between matrix metal and phosphoric ester added into resin solution.

25 Fig. 3 is a diagram of roll-coating equipment which shows coating resin solution on a cold-rolled steel sheet.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of this invention will be explained with
30 reference to the accompanying drawing.

As shown in Fig. 1, the resin-coated steel sheet according to the present invention has a structure that zinc or zinc-nickel is plated on a cold-rolled steel sheet and chromate which contains 100 mg/m² of chrome is treated on the plated steel sheet, and resin solution of the present invention
5 is coated in the thickness of 2-10 μ m.

Low-carbon steel sheet having less than or equal to 0.03% of carbon content is used as the cold-rolled steel sheet in the present invention.

Zinc (Zn), zinc-nickel (Zn-Ni) alloy, zinc-cobalt (Zn-Co) alloy, zinc-manganese (Zn-Mn) alloy or zinc-chrome (Zn-Cr) alloy may be used as the
10 plating material. In the present invention, zinc-nickel (Zn-Ni) alloy steel sheet is preferably used because it has better cosmetic corrosion resistance than that of zinc-plated steel sheet.

Chromate solution applied to zinc-nickel plated steel sheet includes a reactive type, electrolyte type, and coating type, in which coating type is
15 preferable in terms of cosmetic corrosion resistance. When the chromate solution is applied to the steel sheet, it can be plated on one side or both sides. It is preferable to coat on both sides.

However, in case of resin solution, it can be alternatively coated on one side or both sides depending on the needs of consumer.

Such an alternation depends on the welding condition when the resin-coated steel sheet is used for manufacturing fuel tanks. That is, in case of high current condition that is easy for welding and frequent replacing of electrolyte, it is preferable to use steel sheet coated on both sides whereas in case of low current condition and infrequent replacing of electrolyte, it is
20 preferable to use steel sheet coated on one side.

When manufacturing a fuel tank by a steel sheet coated with resin on one side, it is preferable to weld the tank by placing the coated side to face to fuel side and chromate-coated side which is not coated with resin to face to outer side. Thus, it makes welding easily because the welding electrolyte
30 does not contact with resin part. In addition, if necessary, paint is applied to a

side which is not coated with resin in the thickness of about 100 micrometer so to reinforce corrosion resistance of fuel tank, thus, it has little influence to corrosion resistance.

Hereinafter, the resin solution used in the resin-coated steel sheet of
5 the present invention will be explained in detail.

The resin solution of the present invention is prepared by adding at least one of ethylene-acryl resin or phosphoric ester to a basic solution mixed with melamine resin and colloidal silica based on phenoxy resin as a main solution.

10 It is preferable to use a main solution of phenoxy resin having a number average molecular weight of 25,000 to 50,000. When the number average molecular weight is less than 25,000, it is difficult to have desired material properties. When the number average molecular weight is more than 50,000, it is impossible to synthesize the resin due to the limitation of
15 synthetic process.

Phenoxy resin has excellent cosmetic corrosion resistance and fuel corrosion resistance by the following reasons.

The most characteristic property of phenoxy resin is high glass transition temperature(T_g). In case of urethan, epoxy, and acryl resin, glass
20 transition temperature of these is around or less than 50°C , although it depends on the molecular weight. However, glass transition temperature of phenoxy resin is 100°C . High glass transition temperature means high movement temperature of resin chain. Thus, since the resin chains do not show Brown movement below the glass transition temperature, they have
25 primary protecting-effect against outer low molecular corrosion element such as moisture or gasoline. That is, if resin chains show Micro Brown movement, the low molecules easily infiltrate between moving chains so that corrosion elements can easily infiltrate. Therefore, resins with high glass transition temperature have screening effect against matrix metal. Particularly it shows
30 very high screening effect in a flat plane part.

Phenoxy resins, however, have the following shortcomings. That is, since resin coating is very hard, if it is subjected to process, it shows lower drawing than a resin with low glass transition temperature. In addition, since phenoxy resin has a weak adhesion with lower metal coating layer, if it is subjected to process harshly, resin coating is cracked and the adhesion of coating become weaken. Furthermore, if the resin is subjected to process more severe, resin coating exfoliates so that corrosion elements easily infiltrate into the metal coating layer of matrix metal, which results in more corrosion.

10 In manufacturing a fuel tank of an automobile, in order to improve formability during processing, press oil is coated before processing and then the oil is removed. However, the oil removing process makes resin hard. Thus, it cannot expect to have original screening effect because there is damage by the oil removing process in a weak adhesion point. Accordingly, 15 it is preferable to use poly-alloy or poly-blend comprising other resin with good adhesion and drawing ratio than pure phenoxy resin.

The requirements for the other resin forming poly-blend are as follows: First, it has to have compatibility with water-soluble phenoxy resin not to result in gelation or sludge. Second, it does not have influence to the original 20 excellent characteristics of phenoxy resin such as cosmetic corrosion resistance and fuel corrosion resistance and simultaneously it has to lower glass transition temperature of the whole resin, thereby it improves the coating adhesion.

The resin which meets the above requirements is ethylene-acryl resin.

25 There are two methods to add ethylene-acryl resin to phenoxy resin. One is chemical method to bond ethylene-acryl resin to phenoxy resin. The other is physical method. The physical method is preferable.

Since ethylene-acryl resin used in the present invention is synthesized in gas phase and already water-soluble state, it is impossible to synthesize 30 phenoxy resin of water-soluble state and ethylene-acryl resin of water-

soluble state. This is why the chemical method is not appropriate in the present invention.

Ethylene-acryl resin used in the present invention has molecular weight of 20,000 – 50,000. This includes 50 – 80 % of ethylene and 50 – 20 % of acryl resin. If acryl resin is comprised less than 20 %, it is impossible to make a soluble state whereas If acryl resin is comprised more than 80 %, the glass transition temperature becomes high and adhesion becomes poor. The content of ethylene-acryl resin is preferably 5 –15phr(parts per hundred resin). If the content is less than 5phr, coating adhesion effect is less
10 whereas if more than 15phr, fuel corrosion resistance decreases. Since gasoline is a typical carbohydrate compound of carbon and hydrogen, it has very similar structure to ethylene resin comprising carbon and hydrogen, thus gasoline penetrates into ethylene-acryl resin and then is swelled. This is the reason that the fuel corrosion resistance decreases.

15 In order to improve coating adhesion of resin, there is a method to introduce additives other than making poly-blend.

The role of additives reinforces adhesion between phenoxy resin and lower chromate layer during seam processing. Mechanism of phosphoric ester of the additive used in the present invention is explained referring fig. 2.

20 Fig. 2 shows molecular structure of phosphoric ester. Hydroxyl group of phosphoric ester forms hydrogen-bond with hydrogen atom of water molecule, which prevents infiltrating of moisture and improves cosmetic corrosion resistance. Oxygen of phosphoric ester bonds with metal ion of surface layer and improves coating adhesion.

25 The content of phosphoric ester is preferably 0.5-3.0phr on the basis of phenoxy resin. If content of phosphoric ester is less than 0.5phr, the effect of adhesion decreases. If content of phosphoric ester is more than 3.0phr, there is no effect according to the increase of amount.

In order to complement shortcoming of phenoxy resin, it is possible to
30 combine both ethylene-acryl resin and phosphoric ester or combine

optionally. In case of combining both of them, glass transition temperature of phenoxy resin lowers and ions of phosphoric ester bonds with metal, which improve coating adhesion after processing of phenoxy resin.

Furthermore, melamine resin as a hardener can be added to the resin
5 solution of the present invention.

The content of melamine resin is 2-15phr on the basis of phenoxy resin. It is preferable to select melamine resin which has high reactivity. If content of melamine is less than 2phr, hardening reaction is not sufficient after resin coating so that desired physical characteristic is not obtained. On
10 the contrary, if content of melamine is more than 15phr, reactions between hardeners themselves occur so that it adversely influences to the physical characteristics of coating layer.

Further additive added to the resin solution of the present invention is colloidal silica. Colloidal silica is added to improve cosmetic corrosion
15 resistance of resin. The content of colloidal silica is preferably 10-20phr on the basis of phenoxy resin content. If content of colloidal silica is less than 10phr, it is too little to have cosmetic corrosion resistance effect. On the contrary, if content of colloidal silica is more than 20phr, there is no improved effect of cosmetic corrosion resistance relative to the added content of
20 colloidal silica.

Hereinafter, a method of fabricating resin-coated steel sheet using resin solution of the present invention is explained.

The resin-coated steel sheet of the present invention is manufactured by treating chromate on zinc or zinc alloy plated steel sheet, baking drying,
25 coating resin solution and baking drying the steel sheet.

Thickness of the resin coating which is coated on upper side of chromate layer is preferably 2.0-10.0 μm . If the thickness is less than 2.0 μm , the thickness of the coating is too thin to have sufficient cosmetic corrosion resistance and fuel corrosion resistance. On the contrary, if the thickness is
30 more than 10.0 μm , there is no influence to cosmetic corrosion resistance and

fuel corrosion resistance according to increase of the thickness as well as weldability decreases.

Baking temperature after coating the resin solution is preferably 160-250°C based on metal temperature(MT). If baking temperature is less than 5 160°C, hardening reaction of the resin is not sufficient to have cosmetic corrosion resistance and fuel corrosion resistance. On the contrary, if the baking temperature is more than 250°C, hardening reaction does not occur any longer and loss of calories increases.

Coating processes of steel sheet include roll coating, spray, 10 impregnation and so on. It is preferably to use roll coating process in the present invention.

Fig.3 shows roll coating equipment used for treating chromate and coating resin solution. The coating process according to fig.3 comprises dipping resin in a drip pan into pick-up-roll(P.U.R), transferring it by a 15 transfer-roll(T.F.R), dipping it into steel sheet in the applicator-roll(A.p.R), and drying in the oven. The amount of resin attached to the steel sheet is regulated by each roll driving direction, rolling speed, and each roll adhesion pressure.

In the present invention, the above roll coating process can be 20 applicable to one side or both sides of steel sheet.

Now, preferred embodiments are suggested to help the apparent understanding of the present invention. The below embodiments are provided for the sake of clear understanding only and the present invention is not limited thereto.

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Embodiment

Example 1

A composition of phenoxy resin with number average molecular weight of 50,000, 5 phr of melamine resin as a hardener, 15 phr of colloidal 30 silica with particle size 20nm and 2phr of wax is referred to as a standard

solution composition unless other specific note. In addition, the following method is referred to as a standard method of manufacturing steel sheet: treating chromate on electric zinc and zinc alloy plated steel sheet with plate amount of 30g/m^2 , baking drying so as to make metal temperature of 160°C ,
5 cooling it, coating resin solution prepared by various composition, baking drying so as to make metal temperature of 190°C , and forming resin-coated steel sheet with dried coating thickness of $3\mu\text{m}$.

After preparing resin solution by mixing ethylene-acryl resin of which weight ratio is 80:20 of ethylene to acryl with the above standard solution
10 according to the content of below table 1, the resin-coated steel sheet was manufactured by coating the resin solution on the steel sheet plated with zinc of $20\text{-}30\text{g/m}^2$ and treated with chromate of 100mg/m^2 by roll-coating process, baking drying so as to make metal temperature of 190°C , water-cooling and forming resin-coated steel sheet with dried coating thickness of $3\mu\text{m}$.

15 The cosmetic corrosion resistance of the steel sheet prepared by the above process was measured in a processing part by using a salt spray test. A specimen for measurement was prepared by cutting flat plane into 95mm , preparing a cup with diameter of 50mm and height of 25mm , taking out the cup from salt spray after 500 hours, washing with distilled water and drying.
20 According to the amount of occurrence of rust, the grades of cosmetic corrosion resistance were classified in the following way and table 1 showed the result.

Circle in circle (◎): The area of occurrence of white rust is 5% or less with respect to the total area of a specimen.

25 Circle (○): The area of occurrence of white rust is in the range of 5-30% with respect to the total area of a specimen.

Square (□): The area of occurrence of white rust is in the range of 30-50% with respect to the total area of a specimen.

Triangle (△): The area of occurrence of white rust is in the range of
30 50-100% with respect to the total area of a specimen.

In addition, in order to measure coating adhesion after processing, two types of mode were used. The first mode was to measure exfoliated area of resin after detaching cellophane tape that was attached to around of cup specimen with diameter of 50mm and height 25mm cut from flat plane of 95mm. The second mode was to measure the same method as the first mode after applying ultrasound to 10% caustic soda solution for 3 minutes at 50°C and washing. Then, coating adhesion was measured according to the below grades and table 1 showed the result.

Circle in circle (◎): The exfoliated area is 0%.

10 Circle (○): The exfoliated area is 1-5%.

Square (□): The exfoliated area is 5-10%.

Triangle (△): The exfoliated area is 10-20%.

X: The exfoliated area is more than 20%.

Fuel corrosion resistance was measured as follows: A flat plane facing 15 to fuel is cut into 95 mm, and formed to cups with diameter of 50 mm and height of 25 mm. Three kinds of solution of 25ml were poured into the cups. Thereafter, the opening portions of the cups were covered with transparent glass plates by interposing circular "O" rings and fixed with clamp to prevent gasoline from leaking. The solutions were classified into A type, B type and 20 C type. For the A type solution, regular gasoline was mixed with 5% of sodium chloride (NaCl) aqueous solution. For the B type solution, regular gasoline was mixed with 0.2% of sodium chloride. For the C type solution, 85% of regular gasoline was mixed with 14% of methanol and distilled water containing 60ppm of formic acid and 20 ppm of Cl⁻ ion.

25 In order to simulate driving situation of automobile, rocking equipment was used such that the solution contained in the cup was in rocking motion. The cups were allowed to stand for 4 months. Then, the cups were taken out, washed by distilled water, and dried. According to the amount of occurrence of rust, the grades of fuel corrosion resistance were 30 classified in the following way and table 1 showed the result.

Circle in circle (⊙): The area of occurrence of white rust is 5% or less with respect to the total area of a specimen.

Circle (○): The area of occurrence of white rust is in the range of 5-30% with respect to the total area of a specimen.

5 Square (□): The area of occurrence of white rust is in the range of 30-50% with respect to the total area of a specimen.

Triangle (△): The area of occurrence of white rust is in the range of 50-100% with respect to the total area of a specimen.

X: Red rust occurred.

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Table 1

Ex. No.	Main solution	Additive		Hardener		Qualification measurement after processing		
	Type	Type	content	Type	content	Coati ng adhe sion	Cosmetic corrosion resistance	Fuel corrosi on resistan ce
Com.Ex.1	phenoxy resin	Ethyl ene- acryl resin	0	Mela mine resin	5	□	○	○
Com.Ex.2					10			
Com.Ex.3					15			
Com.Ex.4			3		5	○	◎	
Com.Ex.5					10			
Com.Ex.6					15			
Com.Ex.7			20		5	◎		
Com.Ex.8					10			
Com.Ex.9					15			
Ex.1			5		5			◎
Ex.2			10					
Ex.3			15					
Ex.4			5					
Ex.5			10					
Ex.6			15					
Ex.7			5					
Ex.8			10					
Ex.9			15					

The above table 1 shows the result of measurement according to the various contents of ethylene-acryl resin as an additive and melamine resin as a hardener. As can be seen in table 1, when content of ethylene-acryl resin is more than 20phr, coating adhesion and cosmetic corrosion resistance is

good but fuel corrosion resistance decreases. In addition, when ethylene-acryl resin content is less than 5phr, the comparison examples show inferior characteristics to the examples of the present invention.

5 Example 2

After preparing resin solution by mixing phosphoric ester as an additive with the above standard solution according to the content of below table 2, the resin-coated steel sheet was manufactured by coating the resin solution on the steel sheet plated with zinc of 20-30g/m² and treated with
10 100mg/m² of chromate by roll-coating process, baking drying so as to make metal temperature of 190℃, water-cooling and forming resin-coated steel sheet with dried coating thickness of 3μm. After measuring same as Example 1, the result was shown in table 2.

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Table2

Ex. No.	Main solution	additive		hardener		Qualification measurement after processing						
	type	type	content	Type	content	Coating adhesion	Cosmetic corrosion resistance	Fuel corrosion resistance				
Com.Ex. A	Phenoxy resin	Phosphoric ester	0.3	Methylene resin	5	□	○	◎				
Com.Ex. B					10		□					
Com.Ex. C					15				○			
Com.Ex. D			4.0		5	◎	◎					
Com.Ex. E					10							
Com.Ex. F					15							
Ex.A			0.5		5				◎	◎		
Ex.B			1.0									
Ex.C			2.0									
Ex.D			3.0		10						◎	◎
Ex.E			0.5									
Ex.F			1.0									
Ex.G			2.0									
Ex.H			3.0									
Ex.I			0.5		15							
Ex.J			1.0									
Ex.K			2.0									
Ex.L			3.0									

The above table 2 shows the result of measurement according to the various content of phosphoric ester resin as an additive and melamine resin as a hardener. As can be seen in table 2, when content of phosphoric ester resin is in the range of 0.5-3.0phr, coating adhesion after processing is improved. However, when phosphoric ester content is more than 3.0phr or less than 0.5phr, the comparison examples show inferior characteristics to the examples of the present invention.

Meanwhile, when both phosphoric ester and ethylene-acryl resin as additives are mixed to the resin solution of the present invention, it shows the same or excellent effect than that of each additive is mixed as the above examples.

WHAT IS CLAIMED IS:

1. A resin solution used for preparing resin-coated steel sheet for fuel tanks of an automobile comprising:

(i) a main solution of water soluble phenoxy resin having a number
5 average molecular weight of 25,000 to 50,000;

(j) 2 to 15 phr of melamine resin on the basis of said main solution;

(k) 10 to 20 phr of colloidal silica on the basis of said main solution;

and

(l) water soluble ethylene-acryl resin containing 50-80% of ethylene
10 and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000,
in an amount of 5 to 15 phr on the basis of said main solution; and/or 0.5 to
3.0 phr of phosphoric ester on the basis of said main solution.

2. A resin-coated steel sheet for fuel tanks of an automobile coated
with chromate film on cold-rolled steel sheet plated with a zinc (Zn) or zinc-
15 based alloy wherein, the resin solution comprises:

(m) a main solution of water soluble phenoxy resin having a number
average molecular weight of 25,000 to 50,000;

(n) 2 to 15 phr of melamine resin on the basis of said main solution;

(o) 10 to 20 phr of colloidal silica on the basis of said main solution;

20 and

(p) water soluble ethylene-acryl resin containing 50-80% of ethylene
and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000,
in an amount of 5 to 15 phr on the basis of said main solution; and/or 0.5 to
3.0 phr of phosphoric ester on the basis of said main solution,

25 said resin solution coated on said cold-rolled steel sheet with a
thickness of 2–10 μm after drying of the resin coating.

3. A method of fabricating resin-coated steel sheet for a fuel tank of
an automobile comprising the steps of:

coating the resin solution of claim 1 on steel sheet; and

30 baking drying it at 160-250°C so as to have a coating thickness of 2–

10 μm .

4. The method of fabricating resin-coated steel sheet of claim 3, wherein coating process of said resin solution is a roll-coating process.

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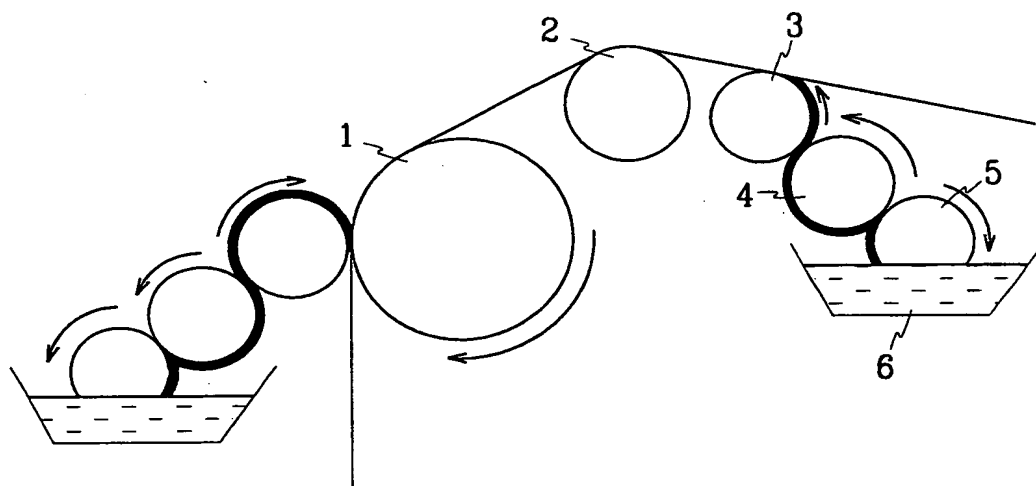
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Fig.3



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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C09D 161/06**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C23C 28/00, B05D 7/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patent and applications for invention since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PAJ, USPTO, NPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 05-156582 A(Nippon Stell Corp.) 22 June 1993 (22.06.93)	1 - 3
A	JP 06-146010 A(Nippon Stell Corp.) 27 May 1994 (27.05.94)	1 - 3
A	US 5397638 A. (Miki et al.) 14 March 1995(14.03.95)	1 - 3

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 MARCH 2001 (12.03.2001)

Date of mailing of the international search report

13 MARCH 2001 (13.03.2001)

Name and mailing address of the ISA/KR

Korean Industrial Property Office
Government Complex-Taejon, Dunsan-dong, So-ku, Taejon
Metropolitan City 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

LIM, Chang Soo

Telephone No. 82-42-481-5582



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR00/01297

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP A2 5156582	22-06-1993	JP B2 2563006	11-12-1996
JP A2 6146010	27-05-1994	-	
US A 5397638	14-03-1995	EP B1 558837	14-08-1996
		JP A2 4197473	17-07-1992
		JP B4 6071579	14-09-1994
		EP A1 558837	08-09-1993

PCT REQUEST

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.91 (updated 10.10.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Korean Industrial Property Office (RO/KR)
0-7	Applicant's or agent's file reference	OPP000860KR
I	Title of invention	RESIN-COATED STEEL SHEET FOR FUEL TANKS OF AUTOMOBILE AND METHOD OF FABRICATING THE SAME
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	POHANG IRON & STEEL CO., LTD.
II-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-city, Kyungsangbuk-do Republic of Korea
II-6	State of nationality	KR
II-7	State of residence	KR
II-8	Telephone No.	82-054-279-6463
II-9	Facsimile No.	82-054-279-6669
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	LEE, Jae-Ryung
III-1-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-1-6	State of nationality	KR
III-1-7	State of residence	KR

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PCT REQUEST

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM


III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	CHANG, Sam-Kyu
III-2-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-2-6	State of nationality	KR
III-2-7	State of residence	KR
III-3	Applicant and/or inventor	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	NOH, Sang-Geol
III-3-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-3-6	State of nationality	KR
III-3-7	State of residence	KR
III-4	Applicant and/or inventor	
III-4-1	This person is:	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	CHO, Soo-Hyoun
III-4-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-4-6	State of nationality	KR
III-4-7	State of residence	KR
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	KIM, Won-Ho
IV-1-2	Address:	Teheran Bldg., 825-33 Yoksam-dong, Kangnam-ku 135-080 Seoul Republic of Korea
IV-1-3	Telephone No.	82-2-3458-0700
IV-1-4	Facsimile No.	82-2-553-5254
IV-1-5	e-mail	email@youme.com
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	CN IN JP US

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PCT REQUEST

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM

V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	12 November 1999 (12.11.1999)
VI-1-2	Number	1999-50110
VI-1-3	Country	KR
VII-1	International Searching Authority Chosen	Korean Industrial Property Office (KIPO) (ISA/KR)
VIII	Check list	number of sheets electronic file(s) attached
VIII-1	Request	4 -
VIII-2	Description	12 -
VIII-3	Claims	2 -
VIII-4	Abstract	1 opp000860kr.txt
VIII-5	Drawings	2 -
VIII-7	TOTAL	21
	Accompanying items	paper document(s) attached electronic file(s) attached
VIII-8	Fee calculation sheet	✓ -
VIII-16	PCT-EASY diskette	- diskette
VIII-18	Figure of the drawings which should accompany the abstract	1
VIII-19	Language of filing of the international application	Korean
IX-1	Signature of applicant or agent	
IX-1-1	Name (LAST, First)	KIM, Won-Ho

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/KR

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PCT REQUEST

OPP000860KR

Original (for **SUBMISSION**) - printed on 13.11.2000 04:52:25 PM

10-6	Transmittal of search copy delayed until search fee is paid	
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FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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PCT (ANNEX - FEE CALCULATION SHEET)

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM

(This sheet is not part of and does not count as a sheet of the international application)

0	For receiving Office use only		
0-1	International Application No.		
0-2	Date stamp of the receiving Office		
0-4	Form - PCT/RO/101 (Annex) PCT Fee Calculation Sheet		
0-4-1	Prepared using	PCT-EASY Version 2.91 (updated 10.10.2000)	
0-9	Applicant's or agent's file reference	OPP000860KR	
2	Applicant	POHANG IRON & STEEL CO., LTD., et al.	
12	Calculation of prescribed fees	fee amount/multiplier	total amounts (KRW)
12-1	Transmittal fee T	⇒	45,000
12-2	Search fee S	⇒	150,000
12-3	International fee Basic fee (first 30 sheets) b1	464,100	
12-4	Remaining sheets	0	
12-5	Additional amount (X)	10,700	
12-6	Total additional amount b2	0	
12-7	b1 + b2 = B	464,100	
12-8	Designation fees Number of designations contained in international application	5	
12-9	Number of designation fees payable (maximum 8)	5	
12-10	Amount of designation fee (X)	100,000	
12-11	Total designation fees D	500,000	
12-12	PCT-EASY fee reduction R	-142,800	
12-13	Total International fee (B+D-R) I	⇒	821,300
12-17	TOTAL FEES PAYABLE (T+S+I+P)	⇒	1,016,300
12-19	Mode of payment	cash	

VALIDATION LOG AND REMARKS

13-2-1	Validation messages Request	Green? A translation of the international application into English will have to be prepared under the responsibility of the ISA selected.
		Green? Please note that the entire request (including the title of invention) must be in English

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PCT (ANNEX - FEE CALCULATION SHEET)

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM

13-2-2	Validation messages States	<p>Green?</p> <p>More designations could be made. The following States have not been designated: AP:(GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW); EA:(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM); OA:(BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG); AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, LI, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW. Please verify.</p>
13-2-4	Validation messages Priority	<p>Yellow!</p> <p>Priority 1: The twelve-month time limit for claiming priority would appear to have expired. Please verify.</p>
13-2-6	Validation messages Contents	<p>Yellow!</p> <p>The power of attorney or a copy of the general power of attorney will need to be furnished unless all applicants sign the request form.</p>
		<p>Green?</p> <p>Priority 1. The priority document is not enclosed. (The applicant must furnish it within 16 months from the earliest priority date claimed)</p>
13-2-10	Validation messages For receiving Office/International Bureau use only	<p>Green?</p> <p>Verify electronic data for consistency against printed form.</p>

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(PATENT COOPERATION TREATY)

발신:수리관청

수신:

KIM, Won Ho

Teheran Bldg., 825-33 Yoksam-dong, Kangnam-ku,
Seoul 135-080, Republic of Korea

PCT



국제출원번호 및 국제출원일 통지서

(PCT 규칙 20.5(C))

발송일
(일/월/년)

21 NOVEMBER 2000 (21.11.2000)

출원인 또는 대리인의 서류참조기호

OPP000860KR

중요통지사항

국제출원번호

PCT/KR00/01297

국제출원일 (일/월/년)

13 NOVEMBER 2000 (13.11.2000)

우선일 (일/월/년)

12 NOVEMBER 1999 (12.11.1999)

출원인

POHANG IRON & STEEL CO., LTD. et al

발명의 명칭

RESIN-COATED STEEL SHEET FOR FUEL TANKS OF AUTOMOBILE AND METHOD OF FABRICATING THE SAME

1. 이 국제출원은 위에 기재된 바와 같이 국제출원번호와 국제출원일이 부여되었습니다.

2. 이 국제출원의 기록원본은:

☐

자로 국제사무국에 송부되었습니다.

☐

아래의 사유로 인하여 아직 국제사무국에 송부되지 않았으며, 이 통지서의 사본은 국제사무국에 송부되었습니다*:

☐

국가안전보장에 필요한 허가를 얻지 못했음

☐

기타 (이유를 상술):

* 국제사무국은 수리관청에 의한 기록원본의 송달을 감시하고 그 접수사실을 출원인에게 통지합니다.
(서식 PCT/IB/301). 국제사무국은 우선일부터 14월이 경과할 때까지 기록원본을 수령하지 않은 때에는 출원인에게 이를 통지합니다. (규칙 22.1(c)).

수리관청명칭 및 우편주소

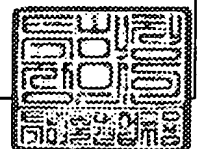
Korean Industrial Property Office
Government Complex-Taejon, Dunsan-dong, So-ku,
Taejon Metropolitan City 302-701, Republic of Korea

팩스번호: 82-42-472-3466

특허청장

COMMISSIONER

전화번호: 82-42-481-5208



서식 PCT/RO/105 (1992년 7월)

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PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference OPP000860KR	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/KR00/01297	International filing date (<i>day/month/year</i>) 13 NOVEMBER 2000 (13.11.2000)	(Earliest) Priority Date (<i>day/month/year</i>) 12 NOVEMBER 1999 (12.11.1999)
Applicant POHANG IRON & STEEL CO., LTD. et al		

This International search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (See Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawing** to be published with the abstract is Figure No. 1-3

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

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RECORD COPY

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PCT REQUEST

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM

0 0-1	For receiving Office use only International Application No.	PCT/KR 00/01291
0-2	International Filing Date	13 november 2000 (13.11.00)
0-3	Name of receiving Office and "PCT International Application"	Korean Industrial Property Office PCT International Application
0-4 0-4-1	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.91 (updated 10.10.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Korean Industrial Property Office (RO/KR)
0-7	Applicant's or agent's file reference	OPP000860KR
I	Title of invention	RESIN-COATED STEEL SHEET FOR FUEL TANKS OF AUTOMOBILE AND METHOD OF FABRICATING THE SAME
II II-1 II-2 II-4 II-5	Applicant This person is: Applicant for Name Address:	applicant only all designated States except US POHANG IRON & STEEL CO., LTD. 1, Koedong-dong, Nam-ku 790-785 Pohang-city, Kyungsangbuk-do Republic of Korea
II-6	State of nationality	KR
II-7	State of residence	KR
II-8	Telephone No.	82-054-279-6463
II-9	Facsimile No.	82-054-279-6669
III-1 III-1-1 III-1-2 III-1-4 III-1-5	Applicant and/or inventor This person is: Applicant for Name (LAST, First) Address:	applicant and inventor US only LEE, Jae-Ryung 1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-1-6	State of nationality	KR
III-1-7	State of residence	KR

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PCT REQUEST

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM


III-2	Applicant and/ r inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	CHANG, Sam-Kyu
III-2-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-2-6	State of nationality	KR
III-2-7	State of residence	KR
III-3	Applicant and/or inventor	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	NOH, Sang-Geol
III-3-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-3-6	State of nationality	KR
III-3-7	State of residence	KR
III-4	Applicant and/or inventor	
III-4-1	This person is:	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	CHO, Soo-Hyoun
III-4-5	Address:	1, Koedong-dong, Nam-ku 790-785 Pohang-shi, Kyungsangbuk-do Republic of Korea
III-4-6	State of nationality	KR
III-4-7	State of residence	KR
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	KIM, Won-Ho
IV-1-2	Address:	Teheran Bldg., 825-33 Yoksam-dong, Kangnam-ku 135-080 Seoul Republic of Korea
IV-1-3	Telephone No.	82-2-3458-0700
IV-1-4	Facsimile No.	82-2-553-5254
IV-1-5	e-mail	email@youme.com
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	CN IN JP US

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PCT REQUEST

OPP000860KR

Original (for SUBMISSION) - printed on 13.11.2000 04:52:25 PM

V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	12 November 1999 (12.11.1999)
VI-1-2	Number	1999-50110
VI-1-3	Country	KR
VII-1	International Searching Authority Chosen	Korean Industrial Property Office (KIPO) (ISA/KR)
VIII	Check list	number of sheets electronic file(s) attached
VIII-1	Request	4 -
VIII-2	Description	12 -
VIII-3	Claims	2 -
VIII-4	Abstract	1 opp000860kr.txt
VIII-5	Drawings	2 -
VIII-7	TOTAL	21
VIII-8	Accompanying items	paper document(s) attached electronic file(s) attached
VIII-8	Fee calculation sheet	✓ -
VIII-16	PCT-EASY diskette	- diskette
VIII-18	Figure of the drawings which should accompany the abstract	1
VIII-19	Language of filing of the international application	Korean
IX-1	Signature of applicant or agent	
IX-1-1	Name (LAST, First)	KIM, Won-Ho

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	13 november 2000 (13.11.00)
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/KR

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PCT REQUEST

OPP000860KR

Original (for **SUBMISSION**) - printed on 13.11.2000 04:52:25 PM

10-6	Transmittal of search copy delayed until search fee is paid	
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FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	08 DEC 2000	(08.12.00)
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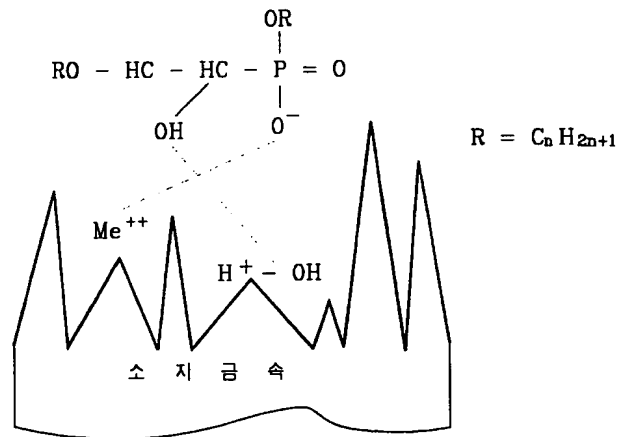
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1/2

도 1

2-5 μ m	수지(페녹시)
50mg/m ²	크로메이트
10-40g/m ²	Zn-Ni 도금
	냉연강판

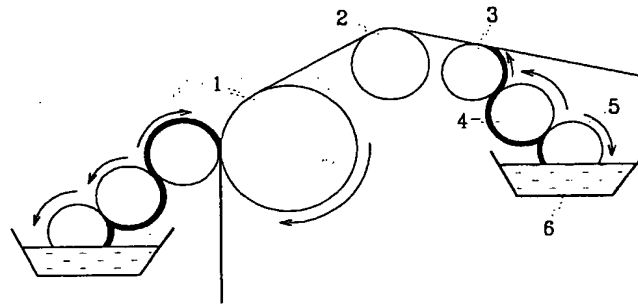
도 2



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자동차 연료탱크 용 수지피복강판 및 그 제조 방법

발명에 대한 배경

(a) 발명이 속하는 기술분야

본 발명은 자동차 연료탱크용 무연 표면처리강판에 관한 것으로서, 보다
 5 상세하게는 크로메이트층이 코팅된 무연 표면처리강판의 표면에 수지용액이 코
 티нг된 수지피복강판 및 이러한 수지피복강판의 제조방법에 관한 것이다.

(b) 종래기술

자동차의 연료를 저장하는 연료탱크(fuel tank)는 대기중의 부식환경에
 견딜 수 있는 내식성(cosmetic corrosion resistance)과 가솔린 등과 같은 연료에
 10 견딜 수 있어야 하는 부식저항성(fuel corrosion resistance)이 요구된다.

또한 강판을 이용하여 연료탱크를 제작할 경우 강판을 프레스하여 상부
 와 하부 두 개의 용기형태로 제작한 다음, 이들 상부와 하부 용기를 맞붙여 연
 결부분을 점(spot) 와 심(seam) 등의 저항용접법으로 용접하거나 솔더링
 (soldering) 또는 브레이징(brazing)과 같은 접합방법으로 접합하여 제작한다. 이
 15 와 같이 자동차용 연료탱크는 두 개의 부품을 맞붙여 접합하기 때문에 자동차용
 연료탱크에 사용되는 강판은 가공성과 용접성이 우수한 재료가 요구된다.

이러한 재료 특성에 적합한 강판 중에 하나가 텀(terne)강판이다. 그러나
 텀강판은 냉연강판에 납-주석을 도금한 것으로 납을 함유한 도금액을 사용하므
 로 강판의 제조시나 사용한 연료탱크를 폐기할 때 납에 의한 환경오염을 유발한
 20 다는 문제점이 있어 그 사용이 규제되어 왔다.

이러한 이유 때문에 납을 사용하지 않는 무연도금강판에 대한 연구가 활
 발히 이루어지고 있다.

납을 사용하지 않는 무연도금강판으로는 본 발명자들이 개발한 국제특허
 공개번호 제 WO 00/32843호가 있다. 이 발명은 아연 및 아연합금 도금강판에
 25 크로메이트 층을 도금하고 그 위에 수지용액을 코팅한 무연도금강판을 사용하여
 내식성과 내연료성을 향상시키고 있다.

상기 발명에서 무연도금강판의 코팅에 사용한 수지용액은 주제용액으로
 페녹시수지를 사용하고 있다. 그러나, 이러한 페녹시수지는 일반 적인 수지보다
 유리전이온도가 높기 때문에 가공을 받지 않는 평판부에서는 에폭시나 아크릴
 30 또는 우레탄수지 등에 비해 내식성 및 내연료성이 우수한 특성을 나타내지만,
 가공부에서는 수지의 높은 유리전이온도의 영향 때문에 심가공시 평판부에 비해

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내식성 및 내연료성이 다소 떨어지는 문제가 있다.

이러한 문제점을 개선하기 위한 방법으로는 폐녹시수지의 유리전이온도를 낮추거나, 폐녹시수지층과 그 하부의 크로메이트층을 화학적으로 결합시켜 심가공시에도 도막이 박리되지 않도록 개선하는 방법 등이 있다.

- 5 폐녹시수지의 유리전이온도를 낮추는 방법으로는 일본 특허 공개번호 평 2-18981호가 있다. 이 발명은 폐녹시수지의 유리전이온도를 하강시켜서 수지분자들을 고무로 변성시켜 수지와 이와 결합하는 하부의 소재와의 도막 밀착력을 강화시키는 방법에 관한 것이다. 그러나 이러한 방법을 수용성수지에 적용할 경우, 고무로 변성할 때 수용화가 어렵고 수용화된 폐녹시수지에 수용화된 고무를
10 투입하기도 어려운 문제가 있다.

발명에 대한 요약

- 본 발명은 이러한 문제점을 개선한 것으로 그 기술적 과제는 수지피복강판의 제조에 사용되는 수지용액을 수지의 물리적 특성을 손상시키지 않고 폐녹시수지의 유리전이온도만을 하강시킬 수 있는 첨가제를 첨가한 수지용액을 제공하
15 는 것이다.

본 발명의 또 다른 목적은 이러한 수지용액을 이용하여 폐녹시수지와 소지금속과의 밀착력을 향상시킬 수 있는 자동차 연료탱크용 수지피복강판의 제조 방법을 제공하는데 있다.

- 이러한 기술적 과제를 달성하기 위한, 본 발명의 특징에 따른 자동차 연료
20 탱크용 표면처리강판을 제조하기 위한 수지용액은

- (a) 수평균 분자량이 25000~50000인 수용성 폐녹시수지의 주제용액;
- (b) 상기 주제용액에 대해 2~12phr의 멜라민수지;
- (c) 상기 주제용액에 대해 10~20phr의 콜로이드 실리카를 포함하고,
여기에
- 25 (d) 분자량이 20000~50000이고, 에틸렌과 아크릴수지가 각각 50~80%, 50~20% 함유된 수용성 에틸렌-아크릴수지를 상기 주제용액에 대해 5~15phr; 그리고/또는 상기 주제용액에 대해 0.5~3.0phr의 인산-에테르;를

혼합하여 이루어져 있다

- 30 본 발명의 또 다른 특징은 아연 또는 아연 합금이 도금된 냉연강판에 크로메이트 피막 처리된 표면처리강판에 있어서,

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- (e) 수평균 분자량이 25000-50000인 수용성 페녹시수지의 주제용액;
- (f) 상기 주제용액에 대해 2~12phr의 멜라민수지;
- (g) 상기 주제용액에 대해 10~20phr의 콜로이달 실리카를 포함하고,
여기에
- 5 (h) 분자량이 20000~50000이고, 에틸렌과 아크릴수지가 각각 50-80%,
50-20% 함유된 수용성 에틸렌-아크릴수지를 상기 주제용액에 대해
5~15phr; 그리고/ 또는 상기 주제용액에 대해 0.5-3.0phr의 인산-
에테르를 혼합하여 이루어진 수지용액을

상기 크로메이트 처리된 냉연강판상에 도포하여 수지피막의 건조후 피막 두께가
10 2-10 μ m 인 자동차 연료탱크용 수지피복강판을 제공함에 있다.

본 발명의 또 다른 특징은 아연 또는 아연 합금이 도금된 냉연강판에 크로
메이트 피막 처리된 표면처리강판을 제조하는 방법에 있어서, 제1항의 수지피복용
액을 도포하여 160-250 $^{\circ}$ C의 소부온도로 건조하여 건조 피막의 두께가 2-10 μ m가
되도록 하는 수지피복단계를 포함하는 자동차 연료탱크용 수지피복강판의 제조
15 방법을 제공함에 있다. 여기서 상기 수지피복용액의 도포 방법은 롤 코팅법으로
도포하는 것이 바람직 하다.

본 발명의 경우 수용성 페녹시수지에 에틸렌-아크릴수지 및 인산-에스테
르를 첨가한 수지피복용액을 제조함으로써, 대폭 향상된 가공후 도막밀착성, 내
연료성, 및 내식성을 지니면서 납이 전혀 사용되지 않는 신도금계 연료탱크강판
20 을 제공하여, 기존 Pb-Sn도금강판 비하여 환경 오염문제를 효과적으 방지할 수
있게 된다. 또한 자동차 연료탱크용 강판의 품질의 향상이 가능하여 수요자의
요구에 충분히 대처할 수 있다.

BRIEF DESCRIPTION OF THE DRAWINGS

도 1은 자동차 연료탱크용 수지피복강판의 피복층을 개략적으로 나타낸
25 단면도이다.

도 2는 본 발명의 수지용액에 첨가되는 인산-에스테르가 소지금속과의 결
합하는 경우를 나타내는 모식도이다.

도 3은 본 발명의 수지용액을 냉연강판에 코팅하는 설비를 나타내는 롤
코팅설비의 개략도이다.

30 발명에 대한 상세한 설명

이하, 본 발명이 속하는 기술 분야에서 통상의 지식을 가진 자가 본 발명
을 용이하게 실시할 수 있는 가장 바람직한 실시예와 첨부된 도면을 이용하여 본

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발명을 상세히 설명한다.

본 발명에 따른 수지피복강판은 도1에서와 같이, 냉연강판상에 아연 또는 아연-니켈 전기도금을 실시하고, 전기도금층이 도금된 강판에, 크롬의 부착량이 $100\text{mg}/\text{m}^2$ 이 되도록 크로메이트 처리한 다음, 본 발명에 의한 수지용액을
5 $2\text{--}10\mu\text{m}$ 가량이 도포되어 있는 구조를 지닌다.

본 발명에서 사용한 기본 강판은 탄소함량이 0.03 % 이하인 저탄소 강으로 냉간가공한 냉연강판을 사용하였다.

이러한 냉연강판의 표면에 도금되는 금속층은 아연(Zn)이나 아연-니켈(Zn-Ni), 아연-코발트(Zn-Co), 아연-망간(Zn-Mn), 아연-크롬(Zn-Cr)등의 아연
10 계 합금을 도금하여 사용할 수 있다. 본 발명에서는 아연만 도금된 것 보다는 내식성이 우수한 아연합금 도금강판인 아연-니켈 강판을 사용하였다.

아연-니켈 도금강판에 도포되는 크로메이트용액은 반응형, 전해형, 도포형이 있는데, 내식성 측면에서 우수한 도포형이 좋다. 크로메이트용액을 도금강판위에 도포할 경우 도금강판의 한 쪽면에서만 도포할 수도 있고 도금강판 양면
15 에 피복할 수도 있지만 양 쪽면에 모두 피복하는 것이 바람직하다.

그러나 본 발명에 의한 수지용액의 경우는 기본적으로 수요자의 요구에 따라 선택적으로 한 쪽면 또는 양 쪽면 모두에 도포하게 된다.

이러한 선택은 본 발명에 의한 수지피복강판을 이용하여 연료탱크를 제작할 경우의 용접조건에 따라 달라진다. 즉, 용접이 용이한 고 전류조건과 전극
20 을 자주 교환하는 경우에는 양 쪽면에 수지가 피복된 강판을 사용하는 것이 바람직하고, 저 전류조건과 전극을 자주 교체하지 않는 경우에는 한 쪽면에만 수지가 피복된 강판을 사용하는 것이 바람직하다.

한 쪽면에만 수지가 피복된 강판으로 연료탱크를 제작하는 경우, 수지피복면이 연료와 맞닿는 쪽으로 향하게 하고 수지가 피복되지 않은 면인 크로메이트만 도포된 면은 바깥쪽으로 향하게 하여 용접하는 것이 바람직하다. 이와 같은 방법으로 용접하게 되면 용접용 전극은 수지가 맞닿지 않는 부분에서 용접을 하게 되어 용접을 쉽게 할 수 있게 된다. 그리고, 수지가 피복되지 않는 면은 필요에 따라 연료탱크의 내식성보강을 위해 두껍게(약 $100\mu\text{m}$) 페인트를 도장 하기 때문에 내식성에 미치는 영향은 거의 없다고 할 수 있다.

30 이하에서는 본 발명의 수지피복강판에 사용한 수지용액에 대하여 상세히 설명한다.

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본 발명의 수지용액은 페녹시수지를 주제용액으로 하여 여기에 멜라민수지와 콜로이달 실리카가 혼합되어 있는 기본용액에 에틸렌-아크릴수지 또는 인산-에스테르를 하나 이상 첨가하여 제조된다.

본 발명의 수지용액에서 주성분인 페녹시수지의 혼합량은 수평균 분자량이 5 이 2만5천-5만인 것이 바람직하다. 수평균 분자량이 2만5천 이하이면 분자량이 너무 적어 원하는 물성확보가 어렵고, 5만 이상이면, 수치합성방법의 한계로 인하여 합성이 불가하기 때문이다.

페녹시수지는 내식성 및 내연료성이 매우 우수한데, 그 이유는 다음과 같다

10 페녹지수지는 다른 수지와는 다른 물리적인 특징을 가지고 있으며, 가장 큰 특성은 유리전이온도(Glass Transition Temperature-Tg)가 높다는 것이다. 즉, 우레탄, 에폭시, 아크릴수지의 경우 분자량에 따라 조금씩은 상이하나 유리전이온도가 대개 50℃부근 또는 그 이하인데 비해, 페녹시수지의 경우 100℃이다. 이와 같이 높은 유리전이온도는 수지사슬이 움직이는 온도가 높다는 것을 의미
15 하는 것으로, 유리전이온도 이하의 온도에서는 수지자체의 사슬들이 마이크로브라운 운동을 하지 않고 그대로 있어 외부 저분자의 부식인자(수분, 휘발유 등)들에 대하여 1차적인 방어효과를 나타낸다. 즉, 수지자체 사슬이 마이크로브라운 운동을 하면 움직이는 사슬사이로 저분자가 쉽게 침투하게 되어 부식인자들의 침투가 용이해 진다는 것이다. 따라서, 높은 유리전이온도의 수지는 그만큼 소지
20 금속에 대한 차폐효과가 커서, 평판상태에서는 상당한 차폐효과를 발휘할 수가 있다.

그러나, 페녹시수지는 상기 장점과 더불어 다음과 같은 문제점도 있다. 즉, 수지도막은 자체가 딱딱(hard)하여, 일단 가공을 받게 되면 연한 수지 즉, 낮은 유리전이온도에 비해 연신이 잘 일어나지 않을 뿐만 아니라 하부의 금속도
25 금속과의 밀착성도 약하기 때문에, 심한 가공시 수지도막이 금이가면서 도막밀착성이 약해진다. 더욱이 좀더 심한 가공에 들어가면 도막이 박리되는 현상까지 일어나 소지금속인 금속도금층에까지 부식인자가 용이하게 침투하여 오히려 부식이 더 잘 일어날 수 있는 가능성이 있다.

자동차의 연료탱크를 제조하는 경우 가공공정에서 성형성을 높이기 위해
30 가공 전에 프레스유를 도포한 다음 프레스하고 이를 제거하기 위하여 탈지공정을 수행하게 된다. 그러나 이와 같이 탈지공정을 하게 되면 수지가 딱딱하여, 도

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막밀착성이 약한 부위에서 탈지액에 의한 손상이 생기므로 수지처리한 원래의 차폐효과를 기대하기가 어렵게 된다. 따라서, 순수한 페녹시수지 보다는 도막밀착성 및 연신율이 우수한 다른 수지를 첨가하여 폴리알로리(poly-alloy) 혹은 폴리 브렌드(poly-blend)상태로 사용하는 것이 바람직하다.

- 5 상기 폴리브렌드를 형성하는 다른 수지의 조건은, 첫째로 수용성 페녹시수지와 상용성이 있어서 젤화나 슬러지가 발생하지 않아야 하고, 두 번째는 페녹시수지 자체가 보유하고 있는 우수한 특성인 내식성 및 내연료성에 영향이 없어야 함과 동시에, 수지전체의 유리전이온도를 낮춤으로써 도막밀착성을 향상시키는 상호 보완적인 효과가 있어야 한다.

- 10 이러한 조건에 부합하는 수지로는 에틸렌-아크릴수지가 있다.

페녹시수지에 에틸렌-아크릴수지를 첨가하는 방식으로는 페녹시수지에 에틸렌-아크릴수지를 화학적으로 결합시키는 방법과 물리적으로 투입하는 방법이 있는데, 여기서는 물리적으로 투입하는 방식이 바람직하다.

- 15 본 발명에서 화학적 결합방식이 적합하지 않은 이유는, 사용되는 에틸렌-아크릴수지가 기상으로 합성이 되고, 이미 수용화된 상태이므로 수용화된 상태의 수지를 수용화된 페녹시수지에 합성하는 것은 불가능하기 때문이다.

- 본 발명에서 사용된 에틸렌-아크릴수지는 분자량이 20000-50000인 것으로, 에틸렌과 아크릴수지가 각각 50-80%, 50-20%함유된 것이 바람직하다. 아크릴수지 가 20%미만으로 함유될 경우 수용화가 안되고, 반대로 80%이상 첨가될 경우 유리전이온도가 높아져 밀착성이 나빠지는 문제가 있기 때문이다. 에틸렌-아크릴수지의 함량은 페녹시수지에 대해 5-15phr(parts per hendred resin: 주제 100중량부당 첨가되는 양) 인 것이 바람직하다. 에틸렌-아크릴수지가 5phr 미만이 되면 도막밀착성 효과가 적고, 반대로 15phr 이상이면, 내연료성이 떨어지게 된다. 내연료성이 떨어지는 이유는 연료로 사용되는 휘발유의 경우 전
20 형적인 탄소와 수소로 구성된 탄화수소화합물이 때문에, 탄소와 수소만으로 된 구조로 구성된 에틸렌수지와 분자구조상으로 유사하여 에틸렌-아크릴수지에 휘발유가 침투하여 팽윤이 일어나기 때문이다.

- 본 발명의 수지용액에 있어서, 수지의 도막밀착성을 향상시키는 방법으로는 상술한 폴리브렌드를 구성하는 방법 외에, 첨가제를 투입하는 방법이 있다.

- 30 첨가제의 역할은 심가공시 페녹시수지와 그 하부층인 크로메이트층과의 밀착력을 강화시키는 것이다. 본 발명에서 사용한 첨가제인 인산-에스테르의 작

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용원리를 도2를 참조하여 간단히 설명한다.

도2는 인산-에스테르의 분자구조를 나타내는 것으로, 인산-에스테르의 수산기는 물 분자의 수소원자와 수소결합을 형성하여 수분이 더 이상 침투하는 것을 막아줌으로써 내식성을 향상시키고, 인산-에스테르의 산소는 표면층의 금속이온과 결합하여 도막밀착성을 향상시켜 준다.

인산-에스테르의 첨가량은 페녹시수지 대비 0.5-3.0phr로 첨가하는 것이 바람직하다. 인산-에스테르의 첨가량이 0.5phr 이하가 되면, 밀착력 향상 효과가 떨어지며 3.0phr 이상이 되면 첨가량이 증가에 따른 효과가 없어지기 때문이다.

본 발명에서는 페녹시수지의 단점을 보완하기 위하여 페녹시수지에 이상 설명한 에틸렌-아크릴수지와 인산-에스테르를 모두 혼합시키거나 선택적으로 혼합시킬 수 있다. 에틸렌-아크릴수지와 인산-에스테르를 모두 혼합시킬 경우 페녹시수지 자체의 유리전이온도가 강하하고 이와 함께 인산-에스테르의 각 이온들이 금속과 결합하여 두 가지가 복합적으로 페녹시수지의 가공 후 도막밀착성을 향상시킬 수 있게 된다.

본 발명의 페녹시수지를 주제용액으로 하는 수지용액에 경화제로서 멜라민수지가 더 첨가된다.

멜라민수지의 첨가량은 페녹시수지 함량 대비 2-15phr 첨가된다. 이 때 첨가되는 멜라민수지의 경우, 반응성이 좋은 것을 선정하는 것이 좋다. 첨가량은 페녹시수지 대비 2phr이하일 경우, 수지피복이 된 후에 경화반응이 충분치 않아 원하는 물리적 특성을 확보하기 어렵게 되고, 반대로 15phr 이상일 경우에는 과량 첨가에 의해 경화제 상호간의 반응으로 피막층의 물리적 특성이 나쁜 영향을 미치기 때문에 바람직하지 않다.

본 발명의 수지용액에 더 첨가되는 물질로는 콜로이달 실리카가 있다. 콜로이달 실리카는 수지의 내식성 향상을 위해 첨가된다. 콜로이달 실리카의 첨가량은 페녹시수지 함량 대비 10-20phr 이 바람직하다. 콜로이달 실리카 함량이 10phr 이하가 되면, 함량이 너무 적어서 내식성효과가 없으며, 반대로 20phr 이상이 되면 실리카 투입함량에 비해 내식성 향상효과가 없기 때문이다.

이하에서는 본 발명의 수지용액을 이용한 수지피복강판의 제조방법에 대하여 설명한다

본 발명의 수지피복강판은, 아연 및 아연합금도금강판에 크로메이트처리

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를 한 다음 소부건조하고, 상기 수지용액을 피복한 후 다시 강판을 소부건조하는 방법으로 제조된다.

크로메이트 층 상부에 도포되는 수지피막의 건조두께는 2.0-10.0 μ m로 하는 것이 바람직하다. 피막의 두께가 2 μ m 이하일 때는 피막두께가 얇아 충분한 내식성과 내연료성을 확보하기가 어렵고, 10 μ m 이상일 때는 피막두께 증가에 따라 내식성과 내연료성에 영향이 없을 뿐 아니라, 강판을 서로 용접할 경우 용접성이 저하되기 때문이다.

상기 수지용액피복후의 소부온도는 강판온도(MT-Metal Temperature)기준으로 160-250°C의 온도범위가 바람직한데, 소부온도가 160°C 이하가 되면, 수지의 경화반응이 충분하지 못하여 내식성 및 내연료성이 저하되며 반대로 250°C 이상이 되면 경화반응은 더 이상 일어나지 않고 열량 손실이 그만큼 크기 때문이다.

한편, 강판의 도포방법으로는 롤에 의한 롤코팅, 스프레이, 침적법등 여러 가지가 있으나 본 발명의 경우는 롤코팅방법을 사용하는 것이 가장 바람직하다.

본 발명의 크로메이트처리 및 수지용액도포에 사용되는 롤 코팅설비는 도 3 과 같다. 도 3에 의한 수지용액도포 방법은 드립팬에 있는 수지를 픽업롤(P.U.R)에 묻혀서 트랜스퍼롤(T.F.R)로 전사후 어프리케이터롤(A.p.R)에서 최종적으로 강판에 묻혀준 뒤 오븐에서 건조하여 수지피막을 형성하는 방법이다. 이 때 부착되는 수지부착량은 각 롤 구동방향, 회전속도, 각 롤 상호 밀착압력 등으로 조절한다.

본 발명에 있어서, 상기한 롤코팅법을 사용하면 강판의 편면 및 양면에 피복 하는 것이 가능하다.

다음은 본 발명의 이해를 돕기 위하여 바람직한 실시예를 제시한다. 그러나 하기의 실시예들은 본 발명을 보다 쉽게 이해하기 위하여 제공되는 것일 뿐 본 발명이 하기의 실시예에 한정되는 것은 아니다.

실시 예1

수평균분자량이 50,000인 페녹시수지에 경화제로서 멜라민 수지를 5phr 첨가한 후 입경이 20nm인 콜로이드 실리카를 15phr, 왁스를 2phr 혼합한 수지용액의 조성 을, 별다른 명기가 없는 한 표준용액조성이라 한다 또한, 도금부착

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량이 30g/m²인 전기아연 및 아연 합금도금강판상에 크로메이트처리를 하고 강판온도가 160℃되게 소부 건조하여 냉각한 후 각각의 조성으로 제조한 수지용액을 도포한 다음 강판온도가 190℃되게 소부건조하여 피막건조두께가 3μm인 수지 피복강판을 제조하는 일련의 공정을 표준강판제조방법이라 한다,

- 5 상기 표준용액조성에, 에틸렌수지 대 아크릴수지의 비율이 80:20인 에틸렌-아크릴수지를 하기 표1과 같은 함량으로 혼합하여 수지용액을 제조한 후, 20-30g/m²의 아연도금부착량으로 도금하고 100mg/m²의 크로메이트처리를 한 강판에 상기 수지용액을 롤코팅방법으로 도포하고, 강판온도가 190℃되게 소부 건조한 다음, 수냉시켜 건조수지 도막두께가 3μm인 수지피복강판을 제조하였다.
- 10 상기한 방법으로 제조된 수지피복강판에 대한 내식성평가는 염수분무시험기를 이용하여 가공부만 평가하였다. 평가를 위한 시편은 평판을 95mm로 절단하여 직경 50mm, 높이 25mm인 컵을 제작한 다음, 500시간이 경과하면 염수분무기에서 반출하여 순수로 세척하고 건조 시켜서 제조하였다. 그 다음, 내식성은 시편에 발생한 녹의 비율에 따라 하기와 같이 평가하고, 그 결과를 아래
- 15 표1에 나타내었다

◎ : 백청 발생면적이 전체 시편 면적 대비 5% 이하

○ : 백청 발생면적이 전체 시편면적 대비 5-30% 이하

□ : 백청 발생면적이 전체 시편 면적 대비 50-50% 이하

△ : 백청 발생면적이 전체 시편 면적 대비 50-100% 이하

- 20 또한, 가공후 도막밀착성 평가를 위해 두가지 모드를 취하였다. 즉, 1차 모드는 평판을 95mm로 절단하여 직경 50mm, 높이 25mm인 컵을 제작한 다음 높이 25mm 컵시편의 둘레에 스카치 테이프를 붙여서 수지가 박리되는 면적으로 구하는 것이고, 2차모드는 50℃, 10% 가성소다용액에 3분간 초음파를 가하여 세척한 다음 1차와 동일하게 평가하여 구하는 것이다. 그 다음, 도막밀착성은
- 25 하기와 같은 기준에 따라 평가하고, 그 결과 역시 표1에 함께 나타내었다.

◎ : 박리된 면적이 0%

○ : 박리된 면적비 1-5%

□ : 박리된 면적이 5-10%

△ : 박리된 면적이 10-20%

- 30 x : 박리된 면적이 20% 이상

내연료성평가는 연료가 맞닿는 부위의 평판을 95mm로 절단하여 직경

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50mm 높이 25mm인 컵을 제작하고, 그 안에 3가지 타입의 용액을 25ml투입한 다음 강판위에 "0"링을 놓고, 그 위에 투명한 유리판을 덮고 클램프로 고정하여 휘발유의 누유를 방지하도록 하였다. 내연료성평가에 사용된 용액은 3가지 종류로 하였는데, A타입의 경우 통상 사용되는 무연휘발유에 5%소금을 혼합한 용액을 사용하였으며, B타입은 통상 사용되는 무연휘발유에 0.2%소금을 혼합한 용액을 사용하였으며, C타입은 메탄올과 첨가제가 함유된 무연휘발유를 그대로 사용하였는데, 상기 C타입의 조성은 무연휘발유85% + 메탄올14% + 개미산60ppm과 CI-20ppm이 함유된 순수1%였다

또한, 자동차의 운행중인 상황을 재현하기 위해, 컵으로 제작된 용기내의 연료가 흔들림을 받도록 미리 제작된 흔들림장치를 이용하였다. 상기 방법의 해 4개월 경과후 반출하여 순수로 세척하고 건조한 다음, 발생한 녹의 비율에 따라 내연료성을 평가한 후, 그 결과를 표1에 나타내었다. 평가기준은 하기와 같다.

- ◎ : 백령 발생면적이 전체 시편 면적대비 5% 이하
○ : 백령 발생면적이 전체 시편 면적대비 5-30% 이하
□ : 백령 발생면적이 전체 시편 면적 대비 30-50% 이하
△ : 백령 발생면적이 전체 시편 면적 대비 50-100% 이하
X : 적청 발생

【표 1】

구분	주제용액	첨가제		경화제		가공후 품질평가		
	종류	종류	함량	종류	함량	도막밀착성	내식성	내연료성
비교재1	페녹시	에틸렌-	0	멜라닌	5	□	○	○
비교재2	수지	아크릴		수지	10			
비교재3		수지			15	△		
비교재4			3		5	○	◎	◎
비교재5					10			
비교재6					15			
비교재7			20		5	◎		□
비교재8					10			○
비교재9					15			

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발명재1			5					
발명재2			10		5			
발명재3			15					
발명재4			5					
발명재5			10		10			◎
발명재6			15					
발명재7			5					
발명재8			10		15			
발명재9			15					

상기 표1에 수지용액중 첨가제인 에틸렌-아크릴수지와 경화제인 멜라민 수지의 함량변화에 따른 품질평가결과가 나타내었다. 표1에서 알 수 있는 바와 같이 에틸렌-아크릴수지 함량이 20phr 이상인 경우, 도막밀착성과 내식성은 양호하였지만, 내연료성은 다소 감소하는 경향을 나타내었다. 또한, 에틸렌-아크릴수지 함량이 5phr 미만인 비교재의 경우도, 각 품질평가에 있어서 본 발명의 발명재보다 나쁜 결과를 나타냄을 알 수 있다.

실시 예2

상기 표준용액조성에 첨가제로 인산-에스테르를 하기 표2와 같은 함량으로 혼합하여 수지용액을 제조한 후, 20-30g/m²의 아연도금부착량으로 도금하고 100mg/m²의 크로메이트처리를 한 강판에 상기 수지용액을 롤코팅방법으로 도포하고 강판온도를 190℃되게 소부건조한 다음 수냉시켜, 건조수지 도막두께가 3 μ m인 수지피복강판을 제조하였다. 그 후 상기 실시예1과 같은 조건으로 품질평가를 실시하여, 그 결과를 표2에 나타내었다.

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【표 2】

구분	주제용액	첨가제		경화제		가공후 품질평가						
	종류	종류	함량	종류	함량	도막밀착성	내식성	내연료성				
비교재A	페녹시수지	인산-에테르	0.3	멜라닌수지	5	<input type="checkbox"/>	○	◎				
비교재B					10		<input type="checkbox"/>					
비교재C					15	○						
비교재D			4.0		5							
비교재E					10							
비교재F					15							
발명재A			0.5		5	◎	◎					
발명재B			1.0									
발명재C			2.0									
발명재D			3.0		10							
발명재E			0.5									
발명재F			1.0									
발명재G			2.0									
발명재H			3.0									
발명재I			0.5		15							
발명재J			1.0									
발명재K			2.0									
발명재L			3.0									

상기 표2에 수지용액중 첨가제인 인산-에스테르와 경화제인 멜라민수지의 함량변화에 따른 품질평가결과가 나타내었다. 상기 표2에서 알 수 있든 바와 같이, 인산에스테르 함량이 본 발명의 0.5-3.0phr 범위내에 있는 경우, 가공후 도막밀착 성이 향상되었다. 그러나, 인산에스테르 함량이 3.0phr 을 초과하거나 0.5hr 미만인 경우, 각 품질평가에 있어서, 본 발명재에 비해 떨어지는 것을 알 수 있다.

한편, 본 발명에 따라 상기 표준용액조성에 첨가제로 인산-에스테르 및 에틸렌-아크릴수지를 복합첨가하면, 상기한 실시예와 같이 인산 에스테르와 에틸렌-아크릴수지를 단독으로 첨가한 것에 비해, 동등이상의 우수한 효과가 있음을 알 수 있었다.

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특허청구범위 :

【청구항 1】

- (i) 수평균 분자량이 25000-50000인 수용성 페녹시수지의 주제용액;
 (j) 상기 주제용액에 대해 2~12phr의 멜라민수지;
 5 (k) 상기 주제용액에 대해 10~20phr의 콜로이달 실리카:를 포함하고,
 여기에
 (l) 분자량이 20000~50000이고, 에틸렌과 아크릴수지가 각각 50-80%,
 50-20% 함유된 수용성 에틸렌-아크릴수지를 상기 주제용액에 대해
 5~15phr; 그리고/ 또는 상기 주제용액에 대해 0.5-3.0phr의 인산-
 10 에테르:를 혼합하여
 이루어지는 자동차 연료탱크용 수지피복강판의 제조에 사용되는 수지용액..

【청구항 2】

- 아연 또는 아연 합금이 도금된 냉연강판위에 크로메이트 피막 처리된 표면
 처리강판에 있어서,
 15 (m) 수평균 분자량이 25000-50000인 수용성 페녹시수지의 주제용액;
 (n) 상기 주제용액에 대해 2~12phr의 멜라민수지;
 (o) 상기 주제용액에 대해 10~20phr의 콜로이달 실리카:를 포함하고,
 여기에
 (p) 분자량이 20000~50000이고, 에틸렌과 아크릴수지가 각각 50-80%,
 20 50-20% 함유된 수용성 에틸렌-아크릴수지를 상기 주제용액에 대해
 5~15phr; 그리고/ 또는 상기 주제용액에 대해 0.5-3.0phr의 인산-
 에테르:를 혼합하여 이루어진 수지용액을
 상기 크로메이트 처리된 냉연강판상에 도포하여 수지피막의 건조후 피막 두께가
 2-10 μ m 인 것을 특징으로 하는 자동차 연료탱크용 수지피복강판.

25 【청구항 3】

- 아연 또는 아연 합금이 도금된 냉연강판에 크로메이트 피막 처리된 표면처
 리강판을 제조하는 방법에 있어서,
 제1항의 수지피복용액을 도포하여 160-250℃의 소부온도로 건조하여 건조 피막
 의 두께가 2-10 μ m가 되도록 하는 수지피복단계를 포함하는 것을 특징으로 하는
 30 자동차 연료탱크용 수지피복강판의 제조방법.

【청구항 4】

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제 3항에 있어서,

상기 수지피복용액의 도포 방법은 롤 코팅법으로 도포하는 것을 특징으로 하는 자동차 연료탱크용 수지피복강판의 제조방법.

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ABSTRACT

The present invention relates to a resin-coated steel sheet for fuel tanks of an automobile and a resin solution used for the same. The resin solution of the present invention comprises (a) a main solution of water soluble phenoxy resin having a number average molecular weight of 25,000 to 50,000; (b) 2 to 15 phr of melamine resin on the basis of the main solution; (c) 10 to 20 phr of colloidal silica on the basis of the main solution, and (d) water soluble ethylene-acryl resin containing 50-80% of ethylene and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000, in an amount of 5 to 15 phr on the basis of the main solution; and/or 0.5 to 3.0 phr of phosphate-ether on the basis of the main solution. The resin solution is coated on a cold rolled steel sheet plated with zinc or zinc alloy over which a chromate layer films, and then dried at a local temperature of 160 to 250 °C to prepare a resin-coated steel sheet for fuel tanks of an automobile.

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